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# $Co^{II}$ and $Rh^{I}$ complexes with $C_2$-symmetric chiral diamines of the dioxolane series

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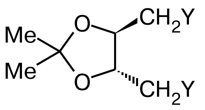
The reaction of di-μ-chlorobis(1,5-cyclooctadiene)dirhodium with (4*S*,5*S*)-2,2-dimethyl-4,5-bis(methylaminomethyl)-1,3-dioxolane (**1**) gave the complex [Rh(cod)(**1**)]Cl (cod is 1,5-cyclooctadiene). The composition of the complexes $CoCl_2 \cdot L_2$ and $[Rh(cod)(L_2)]X$ ($L_2$ = **1**, (4*S*,5*S*)-2,2-dimethyl-4,5-bis(aminomethyl)-1,3-dioxolane, and (4*S*,5*S*)-2,2-dimethyl-4,5-bis(dimethylaminomethyl)-1,3-dioxolane; X = Cl, TfO) was studied using IR and $^1H$ NMR spectroscopy. In the $Rh^I$ cyclooctadienediamine complexes, the diene molecule forms a stronger bond with the metal atom than that in the cyclooctadienediphosphine analogs.

**Key words:** complexes, cobalt(II), rhodium(I), IR spectroscopy, NMR spectroscopy, catalysis by metal complexes.

Transition metal complexes with chiral phosphines are efficiently used in the catalytic synthesis of optically active organic compounds. However, in recent years, considerable attention has been devoted to transition metal complexes with N-donor ligands, namely, amines and imines. These complexes are generally inferior to the phosphine analogs in the chirality transfer to the substrate and in the catalytic activity but are favorably distinguished by the relative simplicity of synthesis and stability against degradation under reductive conditions (in hydrogenation with molecular hydrogen and in hydrogen transfer reactions).[1,2] In particular, $C_2$-symmetric $Co^{II}$ chlorodiamine complexes $CoCl_2 \cdot L_2$ ($L_2$ is (4*S*,5*S*)-2,2-dimethyl-4,5-bis(methylaminomethyl)-1,3-dioxolane (**1**), (4*S*,5*S*)-2,2-dimethyl-4,5-bis(aminomethyl)-1,3-dioxolane (**2**), and (4*S*,5*S*)-2,2-dimethyl-4,5-bis(dimethylaminomethyl)-1,3-dioxolane (**3**)), which are structural analogs of the widely known diphosphine, (*R*,*R*)-(−)-2,2-dimethyl-4,5-bis(diphenylphosphanylmethyl)-1,3-dioxolane (**4**), have demonstrated[3] a moderate chiral induction in the borohydride reduction of acetophenone and esters of unsaturated acids: the optical yield of (*S*)-1-phenylethanol reached 24% *ee* and that of dimethyl (*S*)-α-methylsuccinate was 37.5%. In the catalytic hydrogenation of acetophenone with hydrogen transfer from isopropanol on rhodium chloride and triflate complexes with diamines, $[Rh(L_2)_2]X$ and $[Rh(L_2)(cod)]X$ ($L_2$ = **2**, **3**; X = TfO, Cl), in the presence of KOH and $Bu^tOK$, the optical yield of *S*(−)-2-phenylethanol was 67%.[4]

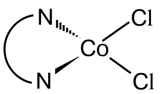


**1—4**

Y = NHMe (**1**), $NH_2$ (**2**), $NMe_2$ (**3**), $PPh_2$ (**4**)

The catalytic activity and the stability of transition metal complexes in solution are determined by numerous factors, in particular, by the nature and the spatial structure of the ligands. Previously, we demonstrated[4] that primary diamine **2** and tertiary diamine **3** form rhodium complexes of different compositions. Therefore, it appeared of interest to try using secondary diamine **1** as the ligand. In this study, we prepared a new rhodium cyclooctadiene chloride complex with diamine **1** and compared characteristics of the $Co^{II}$ and $Rh^I$ complexes with diamines **1—3** by IR and NMR spectroscopy.

## Results and Discussion



$CoCl_2 \cdot L_2$ (**5a—c**)

**$Co^{II}$ complexes with diamines 1—3.** Complexes **5a—c** $CoCl_2 \cdot L_2$ ($L_2$ = **1** (**a**), **2** (**b**), **3** (**c**)) were prepared by the reaction of equimolar amounts of anhydrous $CoCl_2$ and diamines **1—3** in dichloromethane. The metal : ligand ratio in the complexes was 1 : 1, which was confirmed by elemental analysis, indicating the presence of one chiral diamine molecule and two Cl atoms per Co atom. The presence of a single ν(NH) stretching band at 3190 $cm^{-1}$ in the IR spectrum of solid complex **5a** suggests the equivalence of two NH groups and, hence, the chelation mode of ligand coordination. Apparently, similarly to the complexes of cobalt halides with chelated diamines $Me_2N(CH_2)_nNMe_2$ ($n$ = 1—3), which have been studied by X-ray diffrac-

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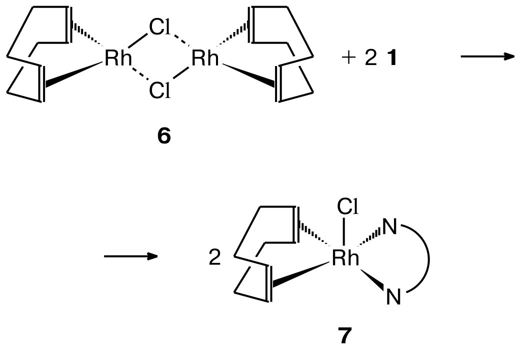
tion,[5] complexes **5a—c** have a tetrahedral geometry. The formation of bridging structures rather than chelates, as in the complexes of metal salts with ethylenediamine,[6] is less likely due to the steric restrictions, caused by the presence of dioxolane rings.

The IR spectrum of free ligand **1** in thin film has two bands at 3335 and 3270 cm$^{-1}$, which is indicative of the nonequivalence of the two NH groups. The IR spectrum of complex **5a** differs sharply from the spectrum of the free ligand by the presence of the single $\nu$(NH) band at 3190 cm$^{-1}$. In the IR spectrum of complex **5b**, the $NH_2$ stretching bands (3316 and 3270 cm$^{-1}$) are also shifted to lower frequencies relative to the bands of the free ligand (3360 and 3290 cm$^{-1}$). The bands at 308 (**5a**) and 307 cm$^{-1}$ (**5b,c**) in the spectra of complexes, which are missing from the spectra of the ligands or $CoCl_2$, are due to vibrations of the Co—N bond. This assignment is consistent with data for a broad range of complexes of amines with cobalt salts.[6]

**Rh$^{I}$ complexes with diamines 1—3.** The reaction of chloride complex $[Rh(cod)Cl]_2$ (**6**) with 2 equiv. of diamine **1** in $CH_2Cl_2$ is accompanied by cleavage of the bridging chloride bonds in dimer **6** to give the yellow-colored complex [Rh(cod)(**1**)]Cl (**7**) (Scheme 1).

**Scheme 1**



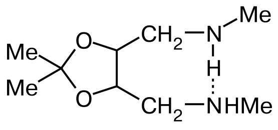
The composition of complex **7** is confirmed by elemental analysis data and the ratio of integral intensities of the proton signals of cyclooctadiene and diamine **1** in the $^1$H NMR spectrum. The pentacoordinated Rh$^{I}$ chlorocyclooctadiene complexes with diamines[7—9] and diphosphines,[10] formed at the $L_2$ : Rh ratio of 1 can have either a trigonal-bipyramidal or a tetragonal-pyramidal geometry. In the solid state, complex **7** exhibits $\nu$(NH) and $\nu$(Rh—N) bands at 3290 and 490 cm$^{-1}$, respectively; this position is typical of rhodium complexes with amines.[6,11,12] The singlet shape of both bands attests to the tetragonal pyramid, as only in this case, both ligands, diamine and diene, are symmetrically related to the central atom, as indicated by the IR and $^1$H NMR data.

The reaction of *N,N*′-dimethylethylenediamine (**8**) with the dinuclear complex **6** results in asymmetric splitting of the bridging chloride bonds to give the $[Rh(cod)(\mathbf{8})]^+[Rh(cod)Cl_2]^-$ ion pair, which typically[7] exhibits two $\nu$(Rh—Cl) bands at 260 and 250 cm$^{-1}$. However, the Rh—Cl stretching band in the spectrum of solid complex **7** is a singlet located at 317 cm$^{-1}$, as in the spectra of Rh$^{I}$ carbonyl complexes with Schiff′s bases or phenanthroline.[13] Thus, the formation of the $[Rh(cod)(\mathbf{1})]^+[Rh(cod)Cl_2]^-$ ion pair upon the reaction of complexes **6** and **1** can be ruled out.

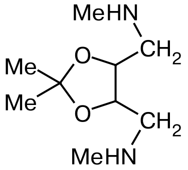
The $\nu$(NH) absorption band for the $[Rh(cod)(\mathbf{2})]^+[TfO]^-$ complex, described in our previous study,[4] occurs at rather low frequencies, 3225 and 3115 cm$^{-1}$. For example, the $\nu$(NH) band for the cationic complexes of 1,5-cyclooctadiene(1,3-propanediamine)rhodium(I) perchlorate[8] and 1,5-cyclooctadiene{(*S*)-1-*tert*-butylaminocarbonyl-2-[(1-naphthylamino)methylpyrrolidine]}rhodium(I) hexafluorophosphate[11] are at higher frequencies (3285, 3240 cm$^{-1}$ and 3420, 3300 cm$^{-1}$, respectively). The lower-frequency shift of the $\nu$(NH) band can be due to the formation of intermolecular hydrogen bonds of the $NH_2$ group of ligand **2** with the $TfO^-$ counter-ion. In the $[Rh(cod)(NH_2(CH_2)_nNH_2)Cl]$ chloride complexes ($n$ = 1—3), which are supposed to contain N—H...Cl hydrogen bonds, the absorption bands occur at even lower frequencies, 3165 and 3070 cm$^{-1}$.[7]

The presence of two $\nu$(NH) bands with similar intensities at 3335 and 3270 cm$^{-1}$ in the IR spectrum of free diamine **1** (see above) is unexpected. Neat diethylamine is known to be completely associated and to be responsible for one IR band at 3270 cm$^{-1}$ due to $\nu$(NH). The second band corresponding to vibrations of the free NH groups of the diethylamine monomer appears only in its solutions in $CCl_4$. This stimulated us to study the spectra of diamine **1** in various media.

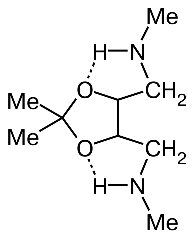
Ligand **1** may exist as conformers **A—D**.



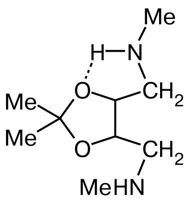
**A**



**B**



**C**



**D**

The IR spectra of dilute solutions of diamine **1** in $CCl_4$, like those of the neat compound, exhibit two $\nu$(NH) bands, namely, a narrow strong band at 3340 cm$^{-1}$ with a half-width of 20 cm$^{-1}$ and a broad weak band at 3275 cm$^{-1}$. A decrease in the concentration of diamine **1** from $1 \cdot 10^{-3}$ to $1 \cdot 10^{-4}$ mol L$^{-1}$ does not change the ratio of their peak intensities. This could be interpreted by assuming that both bands refer to conformer **A**, in particular, the high-frequency band is due to the free NH group, while the low-frequency one, to the NH group involved in the intramolecular NH...N hydrogen bond. However, unlike the vibrations of the free NH groups in diethylamine and other amines, the position of the higher-frequency component of the doublet in the IR spectrum of diamine **1** barely depends on the solvent nature. The shift of this component in various solvents ($CHCl_3$, $C_2H_4Cl_2$, $CH_2Cl_2$, dioxane, $Et_3N$) does not exceed 5 cm$^{-1}$ with respect to $CCl_4$, whereas for diethylamine and other aliphatic amines, the $\Delta\nu$(NH) value is 14 cm$^{-1}$ even in $CHCl_3$, while in dioxane it is as great as 20 cm$^{-1}$, which is due to the formation of an intermolecular hydrogen bond, NH...O, with the solvent.[14] Therefore, it is most reasonable to assign the higher-frequency band to vibrations of the NH group involved in an intramolecular hydrogen bond in conformer **A**, and the lower-frequency band, to vibrations of the NH bond responsible for its self-association. In inert solvents and in protophilic dioxane, conformer **A** predominates, while the content of self-associates changes slightly upon variation of the medium polarity. In neat liquid diamine **1**, the fraction of self-associates is substantially higher. As the temperature of a solution of diamine **1** in $CH_2Cl_2$ decreases from 273 to 170 K, the intensity of the band at 3275 cm$^{-1}$ decreases down to zero at 170 K. Simultaneously, a new low-frequency band appears and grows at ~3200 cm$^{-1}$. This may be related to a more stable polyassociate, as the frequency of this band is lower than that of the corresponding band in the IR spectrum of the 1 : 1 H-complex between diethylamine and triethylamine (3290 cm$^{-1}$). Thus, according to experimental data, conformer **A** is most probable for ligand **1**, while the presence of conformers **B—D** is not confirmed by spectroscopic data.

Chloride complex **7** and the cationic rhodium triflate complexes $[Rh(cod)(\mathbf{2})]^+[TfO]^-$ (**9**) and $[Rh(\mathbf{3})_2]^+[TfO]^-$ (**10**), resulting from the reaction of $[Rh(cod)_2]^+[TfO]^-$ (**11**)[4] with diamines **2** and **3**, respectively, were studied by $^1$H NMR spectroscopy. The chemical shifts of the protons of free and complexed diamines **1—3** in $CDCl_3$ are listed in Table 1. For comparison, the Table presents the $^1$H NMR spectral characteristics of chiral diphosphine **4** (skeletal analog of diamines **1—3**) in the free state and in the cationic complex $[Rh(cod)(\mathbf{4})]^+[TfO]^-$ (**12**).

The ratio of the integral intensities of the proton signals of diamine and diene in complexes **7** and **9** corresponds to 1 : 1 molar ratio. The proton signals of diamines **1—3** shift downfield upon complexation. Meanwhile, the signals for the methylene protons of cyclooctadiene in the rhodium diamine complexes are either slightly shifted upfield ($H_A$) or remain in the same position ($H_B$). The methine protons become nonequivalent (Table 2).

Diamine **3** forms bis-chelate triflate complex **10** with two molecules of **3**, which is confirmed by the lack of cyclooctadiene signals in the $^1$H NMR spectrum and the results of elemental analysis. This suggests a stronger complexing ability of diamine **3** compared to diamines **1** and **2**, resulting in complete displacement of cyclooctadiene from the rhodium coordination sphere.

In the $^1$H NMR spectra of cyclooctadienediamine complexes **7** and **9**, the most pronounced changes are found for the proton signals of the diene =CH fragment,

**Table 1.** $^1$H NMR spectra of diamines **1—3**, diphosphine **4**, and complexes **7**, **9**, **10**, and **12** in $CDCl_3$

| Compound | δ (*J*/Hz)* | | | | | |
|---|---|---|---|---|---|---|
| | $CH_A$ | $CH_B$ | $CH_C$ (m) | NMe (s) | NH (br.s) | $CMe_2$ (s) |
| **1** | 2.75 (dd, $J_{A,C}$ = 3.65, $J_{A,B}$ = 12.2) | 2.71 (dd, $J_{A,B}$ = 12.2, $J_{B,C}$ = 5.62) | 3.89 | 2.45 | 1.48 | 1.39 |
| **2** | 2.89 (dd, $J_{A,C}$ = 3.52, $J_{A,B}$ = 13.2) | 2.81 (dd, $J_{A,B}$ = 13.2, $J_{B,C}$ = 5.92) | 3.77 | — | 1.37 | 1.40 |
| **3** | 2.49 (dd, $J_{A,B}$ = 12.8, $J_{A,C}$ = 6.77) | 2.38 (d, $J_{A,B}$ = 12.7) | 3.77 | 2.21 | — | 1.38 |
| **4** | 2.40 (dd, $J_{A,B}$ = 13.9, $J_{A,C}$ = 4.10) | 2.31 (dd, $J_{A,B}$ = 13.9, $J_{B,C}$ = 6.77) | 3.92 | — | — | 1.33 |
| **7** | 3.02 [0.27] | 2.71 [0] (m) | 3.99 [0.10] | 2.55 [0.10] | 1.99 [0.51] | 1.43 [0.04] |
| **9** | 3.13 [0.24] (d, $J_{A,B}$ = 12.2) | 2.85 [0.04] (dd, $J_{B,C}$ = 6.6, $J_{A,B}$ = 12.2) | 3.95 [0.18] | — | 2.16 [0.79] | 1.39 [−0.01] |
| **10** | 2.89 [0.40] (dd, $J_{A,B}$ = 12.8, $J_{A,C}$ = 2.7) | 2.79 [0.41] (dd, $J_{A,B}$ = 12.8, $J_{B,C}$ = 6.5) | 3.92 [0.15] | 2.58 [0.37] | — | 1.40 [0.02] |
| **12** | 2.72 [0.32] (m) | 2.58 [0.27] (m) | 4.18 [0.26] | — | — | 1.19 [−0.14] |

* The values in brackets are the proton chemical shifts for complexes **7**, **9**, **10**, **12** with respect to the same signals of free ligands **1—4**.

**Table 2.** Proton chemical shifts of the 1,5-cyclooctadiene fragment in $Rh^I$ complexes in $CDCl_3$

| Compound | δ* | | |
|---|---|---|---|
| | CH | $CH_A$ (m) | $CH_B$ (m) |
| **6** | 4.22 | 2.49 | 1.74 |
| **7** | 4.32 [0.10],<br>4.08 [−0.14] | 2.39 [−0.10] | 1.75 [0.01] |
| **9** | 3.95 [−0.21] (br.s),<br>4.21 [0.05] (br.s) | 2.43 [0] | 1.82 [0] |
| **11** | 4.16 (m) | 2.43 | 1.82 |
| **12** | 4.52 [0.36] (m),<br>4.28 [0.12] (m) | 2.29 [−0.14] | 2.13 [0.31] |

* The values in brackets are the proton chemical shifts in the obtained complexes **7**, **9**, **12** with respect to the same signals for the starting complexes **6**, **11**.

which become nonequivalent upon coordination with the diamine. The positions of the $CH_A$ and $CH_B$ proton signals in the coordinated diene molecule almost do not change (see Table 2). The coordination of diphosphine **4** to rhodium influences the cyclooctadiene chemical shifts in a different way: the signals of the methylene protons move toward each other, while the signals of the methine protons undergo a substantial downfield shift, which is indicative of weakening of the binding between the diene molecule and the metal atom.

The binding of an olefin to a transition metal is known[15] to involve both the formation of a donor—acceptor σ-bond and the back donation due to interaction of the metal $d_\pi$-orbital with the diene π*-orbital. The coordination of diamines **1—3** to the rhodium atom has little influence on the electron density distribution in the diene molecule. Conversely, the coordination bond with the diphosphine ligand weakens the binding between the diene molecule and the rhodium atom, which is manifested as a downfield shift of the =CH protons and indicates an increase in the C=C bond order in the diene molecule. The observed pattern is consistent with the fact that in the case of diamines **1—3**, the ligands behave as hard bases, whereas diphosphine **4** as a ligand acts as a soft bases.

The stronger diene binding in the $Rh^I$ cyclooctadiene diamine complexes compared to the cyclooctadiene diphosphine complexes results in inhibition of the activation step of the hydrogen molecule by these complexes, which accounts for the lower catalytic activity of the former in hydrogenation of methyl α-acetyl-*N*-amidocinnamate and dimethyl itaconate.[16]

## Experimental

IR spectra of solid (in mineral oil) and liquid (in thin film) compounds and their solutions were recorded on Specord 75 IR and Specord M-82 spectrophotometers in the 4000—400 and 400—200 $cm^{-1}$ ranges, respectively. IR spectra were measured in $CH_2Cl_2$ in the temperature range from 273 to 170 K using a thermostated cell. The $^1H$ NMR spectra were recorded on a Bruker DPX-400 spectrometer (400 MHz) in $CDCl_3$, $CD_3OD$, $C_6D_6$ or acetone-$d_6$, the chemical shifts were referred to the residual proton signals of the solvent.

The solvents used ($CCl_4$, $CHCl_3$, $CH_2Cl_2$, $C_2H_4Cl_2$, dioxane, and $Et_3N$) were purified by known procedures.[17] Diamines **1—3** were prepared as described previously.[18—20] Complexes **5a—c** were synthesized by a known procedure.[3]

**(1,5-Cyclooctadiene)[(4*S*,5*S*)-2,2-dimethyl-4,5-bis(methylaminomethyl)-1,3-dioxolane]rhodium(I) chloride (7).** Diamine **1** (92.5 mg, 0.578 mmol) in $CHCl_3$ (3 mL) was added with stirring under argon to a solution of complex **6** (135 mg, 0.289 mmol) in $CHCl_3$ (30 mL). After 1 h, the resulting light-brown solution was concentrated under reduced pressure to 3 mL, hexane (3 mL) was added, and the light yellow precipitate was washed with hexane (3×5 mL) and dried for 2 h (30 °C (1 Torr)). Found (%): C, 48.11; H, 7.32; Cl, 7.54; N, 6.08. $C_{18}H_{32}ClN_2O_2Rh$. Calculated (%): C, 48.39; H, 7.22; Cl, 7.93; N, 6.27. IR, ν/$cm^{-1}$: 3290 (NH), 490 (Rh—N), 317 (Rh—Cl).

**(1,5-Cyclooctadiene)[(4*S*,5*S*)-2,2-dimethyl-4,5-bis(aminomethyl)-1,3-dioxolane]rhodium(I) triflate (9).** A solution of diamine **2** (92.5 mg, 0.578 mmol) in $CHCl_3$ (3 mL) was added with stirring under argon to a solution of complex **11** (135 mg, 0.289 mmol) in $CHCl_3$ (30 mL). After 1 h, the light-brown precipitate was concentrated to 3 mL at a reduced pressure, hexane (3 mL) was added, and the light yellow precipitate was washed with hexane (3×5 mL) and dried for 2 h (30 °C (1 Torr)). Found (%): C, 37.11; H, 5.62; F, 10.20; N, 6.08; S, 6.08. $C_{16}H_{28}F_3N_2O_5RhS$. Calculated (%): C, 36.93; H, 5.42; F, 10.95; N, 5.38; S, 6.16. IR, ν/$cm^{-1}$: 3225, 3115 both br (NH).

**Bis[(4*S*,5*S*)-2,2-dimethyl-4,5-bis(dimethylaminomethyl)-1,3-dioxolane]rhodium(I) triflate (10).** Silver triflate (25.7 mg, 0.1 mmol) was added to a mixture of complex **6** (0.05 mmol) and cyclooctadiene (0.1 mmol) in degassed acetone (50 mL). The AgCl precipitate formed was filtered off, and 1.2 equiv. of diamine **3** (27.6 mg, 0.127 mmol) in acetone (3 mL) was added to the remaining yellow solution of $[Rh(cod)_2]^+[TfO]^-$. The resulting solution was concentrated to 3 mL, and the complex was precipitated with diethyl ether, washed successively with diethyl ether and hexane, dried *in vacuo*, and stored in a sealed tube. Yield 0.04 g (60%), m.p. 128—132 °C. Found (%): C, 40.81; H, 7.62; F, 7.92; N, 8.08; S, 4.38. $C_{23}H_{48}F_3N_4O_7RhS$. Calculated (%): C, 40.29; H, 7.20; F, 8.31; N, 8.17; S, 4.68. $^1H$ NMR ($CD_3OD : C_6D_6 = 1 : 4$), δ: 1.38 (s, 6 H, $Me_2C$); 2.47 (s, 12 H, $NMe_2$); 2.79 (dd, 2 H, $H_A$ in $CH_2$, $^3J_{H,H}$ = 6.59 Hz, $^2J_{H_A,H_B}$ = 13.2 Hz); 2.88 (d, 2 H, $H_B$ in $CH_2$, $^2J_{H_A,H_B}$ = 13.1 Hz); 3.90 (m, 2 H, CH). $^1H$ NMR (acetone-$d_6$), δ: 1.36 (s, 6 H, $Me_2C$); 2.68 (s, 12 H, $NMe_2$); 2.75 (m, 2 H, $CH_2$); 3.89 (m, 2 H, CH). $^{13}C$ NMR (acetone-$d_6$), δ: 27.23 ($C\underline{C}H_3$); 45.68 ($NCH_3$); 60.60 ($CH_2$); 77.90 (CH). $^{13}C$ NMR ($CD_3OD + C_6D_6$), δ: 27.23 ($C\underline{C}H_3$); 45.19 ($NCH_3$); 60.93 ($CH_2$); 77.20 (CH); 109.11, 111.85 ($\underline{C}CH_3$). $^{19}F$ ($CD_3OD$), δ: 76.99.

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